

ELECTROLYTIC REDUCTION OF SPENT OXIDE FUEL - BENCH-SCALE TEST PREPARATIONS

by

Steven D. Herrmann, Shelly X. Li, Michael F. Simpson, and Dale R. Wahlquist*

Engineering Technology Division
Argonne National Laboratory-West
P. O. Box 2528
Idaho Falls, ID 83403-2528

The submitted manuscript has been created by the University of Chicago as Operator of Argonne National Laboratory ("Argonne") under contract No. W-31-109-ENG-38 with the U.S. Department of Energy. The U.S. Government retains for itself, and others acting on its behalf, a paid-up nonexclusive, irrevocable worldwide license in said article to reproduce, prepare derivative works, distribute copies to the public, and perform publicly and display publicly, by or on behalf of the Government.

To be Presented
at ANS Fifth Topical Meeting on DOE Spent Nuclear Fuel
and Fissile Materials Management

Charleston, SC

September 17 - 20, 2002

*Work supported by the U.S. Department of Energy, Office of Nuclear Energy, Science and Technology, and the Office of Environmental Management, under Contract W-31-109-Eng-38.

Electrolytic Reduction of Spent Oxide Fuel – Bench-Scale Test Preparations

Steven D. Herrmann
Argonne National
Lab.
P.O. Box 2528
Idaho Falls, ID 83403

Shelly X. Li
Argonne National
Lab.
P.O. Box 2528
Idaho Falls, ID 83403

Michael F. Simpson
Argonne National Lab.
P.O. Box 2528
Idaho Falls, ID 83403

Dale R. Wahlquist
Argonne National
Lab.
P.O. Box 2528
Idaho Falls, ID 83403

ABSTRACT

Preparations are underway to demonstrate the electrolytic reduction of spent oxide nuclear fuel in the Hot Fuel Examination Facility (HFEF) at Argonne National Laboratory – West (ANL-W). The electrolytic reduction process, developed by the Laboratory's Chemical Technology Division, operates in an electrochemical cell that uses a molten solution of lithium chloride and dissolved lithium oxide as the electrolyte. The spent oxide fuel is loaded into a permeable steel basket as the cathode in the electrochemical cell and a platinum electrode functions as the anode. When an electrical potential is applied, the uranium oxide and other metal oxides are reduced to metal and remain in the cathode basket. Oxygen gas is formed at the platinum anode and dissipates into the system's argon atmosphere. Once reduced to metal, the spent fuel is capable of further electrometallurgical treatment in an electrolytic cell to recover uranium and to ultimately effect the disposition of fission products into ceramic and metal waste forms. Thus, the electrolytic reduction process expands the electrometallurgical treatment capability to include spent oxide fuel. This report describes the bench-scale test preparations that are underway to demonstrate the electrolytic reduction of spent oxide fuel.

INTRODUCTION

Electrometallurgical treatment of sodium bonded spent metal fuel has been proven at ANL-W and operations are underway to treat a total of 26 MTHM of Experimental Breeder Reactor-II and other sodium bonded spent fuel over the next several years. The bench-scale experiments described in this paper are meant as proof of concept for planning a larger-scale demonstration of an integrated electrolytic reduction and electrometallurgical treatment of spent oxide fuel. The characteristics of the fuel

for the bench-scale demonstration are typical of those for a spent light water reactor fuel with an average burn-up of 4.5 at% and a 24-yr decay. The uranium oxide fuel with Zircaloy-4 cladding was irradiated in Belgium Reactor-3 (BR-3) in Mol, Belgium. The fuel will be declad and crushed to defined ranges of particle size. Chemical and isotopic analysis of the fuel will be performed prior to subjecting it to electrolytic reduction. Post-test examinations for this demonstration include 1) the partitioning of fuel constituents between the liquid and solid phases, 2) the extent of reduction of metal oxides in the fuel basket, and 3) the compounds of metal oxides remaining in the fuel basket.

TEST OBJECTIVES

The purpose of the bench-scale tests is to demonstrate the electrolytic reduction of spent oxide fuel in the Hot Fuel Dissolution Apparatus (HFDA) at HFEF with BR-3 fuel, presently in storage at ANL-W. The scope of work for these tests involves 1) retrieving the BR-3 spent oxide fuel from storage and transporting individual BR-3 fuel elements into the HFEF main cell, 2) removing the cladding, 3) crushing and sieving the fuel into particle size ranges between 45 μm and 4 mm, 4) performing chemical and isotopic analysis of the fuel, 5) loading the fuel into baskets and effecting its electrolytic reduction in the HFDA, and 6) performing post-test analyses on the salt and fuel.

A nominal spent oxide fuel loading for an electrolytic reduction run in the HFDA is 50 g of heavy metal (HM). A sufficient number of electrolytic reduction runs will be performed in order to treat the spent oxide fuel from an entire BR-3 element, i.e. approximately 10 runs per BR-3 element. Prior to electrolytic reduction of *spent* oxide fuel, the HFDA and associated equipment and processes will be validated with *unirradiated* depleted uranium oxide fuel.

Specific objectives of the equipment and process validation with *unirradiated* depleted uranium oxide fuel include 1) establishing the electrochemical cell conditions to effect uranium oxide reduction, and 2) determining the benefit of rotating the fuel basket during electrolytic reduction. Specific objectives of the experimental study with *spent* oxide fuel include 1) quantifying the partitioning of fuel constituents between the liquid and solid phases, 2) determining the rate and extent of reduction of metal oxides in the fuel basket and consequent current efficiency, and 3) identifying the compounds of metal oxides remaining in the fuel basket, e.g. rare earth oxides.

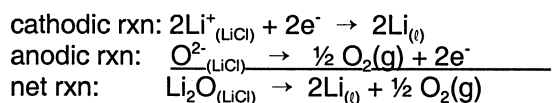
PROCESS DESCRIPTION

The *electrolytic* reduction of oxide fuel has evolved from the *chemical* reduction of uranium oxide in a lithium-based salt system. However, in order to understand the limitations of the former technique, a brief description of the latter comes first. Additional information on the lithium-based chemical reduction process has been reported.¹

Both the electrolytic and chemical reduction processes for oxide fuel operate with lithium chloride at 650°C, which is slightly above the salt's melting point of 610°C. In the chemical reduction process, an excess of lithium metal is introduced into the system, a portion of which is soluble (i.e. 0.08 wt%) in the lithium chloride. Thus, the bulk of the lithium is a separate liquid phase. When a permeable basket loaded with uranium oxide is introduced, the soluble lithium chemically reduces the uranium oxide to metal via the following reaction.



The resultant lithium oxide accumulates in the salt as a soluble species. In a separate electrowinning process, the lithium is recovered via decomposition of the lithium oxide in the salt at 650°C via the following reactions.



Molten lithium metal accumulates at a cathode

(typically a porous stainless steel) and the oxygen gas forms at an inert anode (typically platinum) and dissipates into the system's atmosphere. The standard potential (E°) for decomposition of lithium oxide at 650°C is -2.47 V, while that for lithium chloride is -3.46 V. However, the cell voltage (E) is a function of the activities of the reacting species, as expressed by the standard Nernst equation below.

$$E = E^\circ - \frac{RT}{2\mathcal{F}} \ln \frac{a_{\text{Li}_{(\text{l})}}^2 a_{\text{O}_2(\text{g})}^{1/2}}{a_{\text{Li}_2\text{O}_{(\text{LiCl})}}} \quad (2)$$

where: E° = emf under standard state conditions; $E^\circ = -\Delta G^\circ_{\text{Li}_2\text{O}}/2\mathcal{F}$

$\Delta G^\circ_{\text{Li}_2\text{O}}$ = standard state formation energy of Li_2O at the cell operating temp.

\mathcal{F} = Faraday constant

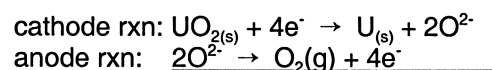
R = gas constant

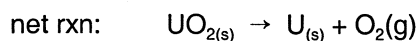
T = temperature

a = activities of the reacting species in the system, i.e. $\text{Li}_{(\text{l})}$, $\text{O}_2(\text{g})$, and $\text{Li}_2\text{O}_{(\text{LiCl})}$

Consequently, as the decomposition of lithium oxide proceeds, the oxygen ion activity decreases and the magnitude of the cell voltage increases. To complicate matters further, the observed cell voltage (E_{obs}), which is the voltage observed from the electrochemical cell potentiometer, will reflect a number of less defined overpotentials, including junction potentials and ohmic losses. Consequently, the magnitude of the observed cell voltage is additionally larger than the standard potentials.

In contrast to the above described *chemical* reduction process and integral electrowinning step, the *electrolytic* reduction process is operated for direct electrochemical decomposition of uranium oxide. Specifically, oxide fuel is loaded into a current carrying steel basket as the cathode and submerged into a lithium chloride - 1 wt% lithium oxide solution at 650°C. With an inert anode (typically platinum) in contact with the salt solution, an appropriate potential across the cell will decompose the uranium oxide to metal via the following overall reactions.





Uranium metal remains in the cathode basket and the oxygen gas dissipates into the system's atmosphere. The standard potential (E°) for decomposition of uranium oxide at 650°C is -2.40 V, which is only 75 mV less in magnitude than the standard potential for lithium oxide. This relatively narrow operating voltage window between the decomposition of the two major oxides in the system can make it difficult to preclude any lithium production when operating such a cell. A controlled production of lithium from lithium oxide should not be detrimental to the system, since it would merely contribute to the chemical reduction of uranium oxide. However, a potential downside to lithium production is that if its production rate sufficiently exceeds its reaction rate with uranium oxide, insoluble lithium droplets could form and attack the platinum anode. Previous bench-scale electrolytic reduction tests suggest that the attack on platinum by lithium is quick (on the order of minutes) and can completely open the electrochemical circuit. Additional observations from the electrolytic reduction of uranium oxide are documented.²

The narrow voltage margin between electrochemical decomposition of uranium oxide and lithium oxide results in the potential for simultaneous *chemical* and *electrolytic* reduction of oxide fuel. In light of this understanding, the demonstration of the electrolytic reduction process in the subject tests will seek to 1) limit the production of lithium, and 2) maintain a constant lithium oxide concentration. Indeed, the purpose of the electrolytic reduction of unirradiated depleted uranium oxide is largely to establish the operating conditions to meet these two operating criteria, prior to proceeding with the spent oxide fuel demonstration.

TEST MATERIALS AND EQUIPMENT

BR-3 Spent Oxide Fuel

In 1984 ANL-W received spent oxide fuel elements from the Belgium Reactor - 3 (BR-3), a light water reactor operated by Belgonucleaire, for examination and testing.³ The electrolytic reduction process will be demonstrated with one of these spent oxide fuel elements. A schematic of a BR-3 fuel element

is shown in Figure 1 and fuel element fabrication characteristics are listed in Table I. The fuel compositions from segments of a typical BR-3 fuel element are shown in Table II. Table I. BR-3 Fuel Element Fabrication Characteristics

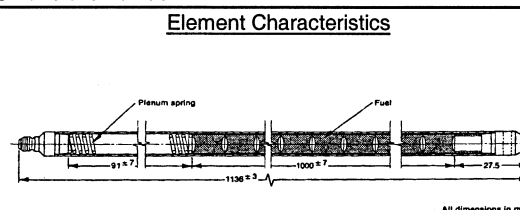


Figure 1. Sectional View of a BR-3 Fuel Element

Length	1.136 m
Diameter	9.5 mm
Cladding thickness	0.57 mm
Fuel stack length	1.000 ± 0.007 m

Fuel Characteristics

Diameter	0.804 cm
Linear density	5.18 ± 0.13 g/cm
Mass density	10.202 g/cc
Total UO_2 mass	535 g/rod
Total U mass	471 g/rod
U-234 composition	0.063 wt%
U-235 composition	8.253 wt%
U-236 composition	0.052 wt%
U-238 composition	91.632 wt%

Table II. Fuel Composition of a Spent BR-3 Fuel Element

	Pellet 1 (12 cm above center)	Pellet 2 (4 cm below center)	Pellet 3 (20 cm below center)
Total U	8.572 g	8.304 g	6.784 g
Total Pu	60.33 mg	59.18 mg	47.72 mg
Isotopic U at%			
U-234	0.052	0.051	0.052
U-235	3.994	3.802	4.183
U-236	0.900	0.934	0.864
U-238	95.054	95.212	94.901
Isotopic Pu at%			
Pu-239	67.74	66.81	68.78
Pu-240	23.52	24.16	22.55
Pu-241	8.74	9.03	8.67
Burn-up	4.44 at%	4.68 at%	4.26 at%

Fuel Preparation Equipment

Fuel preparation equipment for this experimental study is required to 1) cut open a BR-3 fuel element, 2) crush the fuel, and 3) sieve the fuel. Segmenting of a BR-3 fuel element will be performed with a cutting tool that does not crimp the cladding. A slide hammer has been fabricated to crush the fuel, and an existing shaker (Gilson, Model No. SS-5) will be used for sieving. Three inch round stainless steel sieves will be used for sieving the fuel into 4 particle size ranges, i.e. $45\mu\text{m}$ to 0.6 mm, 0.6 mm to 1.2 mm, 1.2 mm to 2.8 mm, 2.8 mm to 4.0 mm. The $<45\mu\text{m}$ fines will be collected for sample analysis.

Hot Fuel Dissolution Apparatus

The HFDA has operated in HFEF for several years as an electrorefiner in the development of the electrometallurgical treatment process for spent metal fuel. The HFDA has been modified slightly to accommodate the electrolytic reduction of oxide fuel, utilizing the five available ports through the vessel head and heat shields to access the salt pool, as shown in Figure 2.

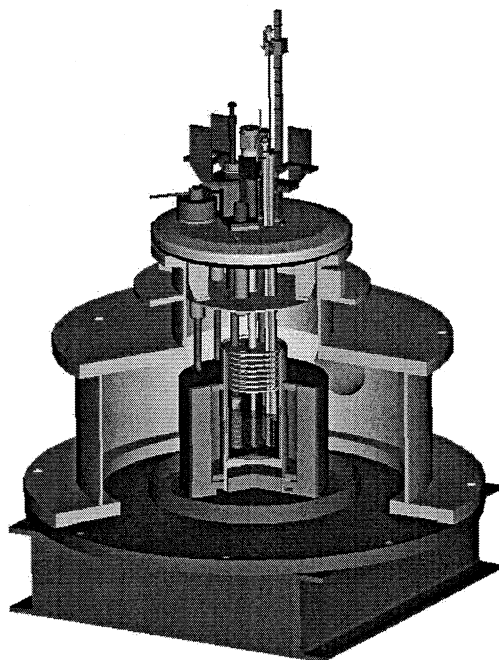


Figure 2. Sectional View of HFDA

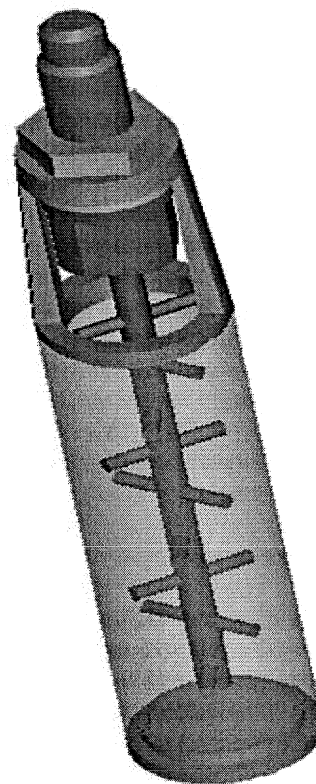


Figure 3. HFDA Cathode Fuel Basket

The HFDA crucible is fitted with a magnesia liner (4 in. OD x 4.5 in., Ozark Technical Ceramics) to electrically isolate the salt from ground. The fuel basket is configured with a 325 mesh lined outer wall, concentric to a multi-pronged, current conducting rod, as shown in Figure 3. The anode is configured with a 1 mm dia. platinum wire concentric to a 3/8 in. dia. magnesia tube. Approximately 1/4 in. of the bottom of the magnesia tube contacts the salt and the platinum wire extends past the end of the magnesia tube and into the salt approximately 2 inches. A 1/4 in. dia. reference electrode is co-located with the anode, i.e. the anode and reference electrodes are separated by a finite distance, but share the same port. A second identical reference electrode occupies an adjacent port. Both reference electrodes provide a Ni/NiO junction in electrolytic contact with the salt. The central thermocouple well has been modified so that it is electrically isolated (ungrounded) from the HFDA vessel.

Electrochemical Instrumentation

The same electrochemical instrumentation that is used to run the HFDA as an electrorefiner will be used for demonstrating the electrolytic reduction of spent oxide fuel, i.e. a potentiostat (EG&G, Model 273A), a power booster (KEPCO, Bipolar Operational Power Supply/Amplifier), and a data acquisition system and associated software (HP, Model No. 34970A).

TEST PLANS

Test Procedure

A magnesia lined crucible will be loaded with approximately 750 g of lithium chloride (initial tests will use a salt purity of 99.99% and <100 ppm moisture) and 1 wt % lithium oxide and melted in the HFDA to produce approximately 500 ml of molten salt with a 3 in. salt height. Approximately 50 g HM of crushed BR-3 fuel will be loaded into a cathode basket. The basket will be loaded into the HFDA along with the anode, reference electrodes, and TC well. A potential will be applied across the anode and cathode in a manner to electrolytically decompose the uranium oxide while minimizing or restricting lithium oxide decomposition. Once the reduction is complete, the anode will be removed from the HFDA, a salt sample will be withdrawn, and the cathode basket will be removed.

Post-Test Analysis

Following an electrolytic reduction run, the salt sample and the entire cathode basket will be submitted to the ANL-W Analytical Laboratory for chemical and isotopic analyses. The expected and possible distribution of fuel constituents from an electrolytic reduction run are depicted in Figure 4. Specifically, the uranium and transuranic oxides are expected to be reduced to metal and remain in the cathode basket. The noble metal fission products, e.g. Zr, Mo, Ru, Pd, Tc, are expected to be reduced to metal (if not already) and to likewise remain in the cathode basket. The fission product alkali and alkali-earth constituents, e.g. Cs, Ba, Sr, Rb, along with those capable of forming salt soluble compounds with lithium, e.g. Te, I, Se, Br, are expected to enter the salt phase. The majority of the rare earths, e.g. Nd, Ce, La, Pr,

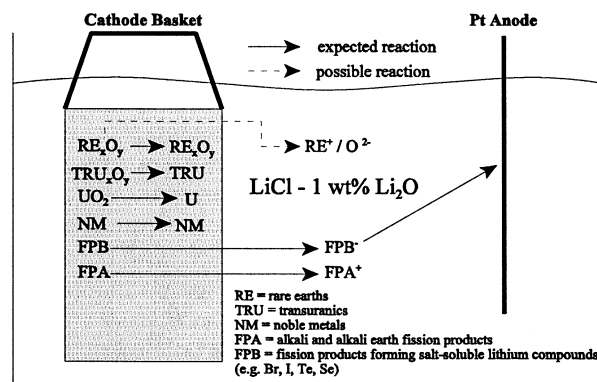


Figure 4. Distribution of Fuel Constituents from Electrolytic Reduction of Spent Oxide Fuel

Sm, Y, are not expected to be reduced and should remain in the fuel basket. However, some of the rare earths could enter the salt phase as soluble oxide species. Another possible complication is plate-out or attack of Te or Se on the platinum anode. Thus, analysis of the platinum anode wire for such constituents may be performed.

The entire fuel basket will be subjected to analysis, in order to determine the composition of fuel constituents between the metal and oxide phases within the basket. These compositions will reveal how effectively the lithium-based electrolytic reduction reduces spent oxide fuel constituents. The salt sample will examine the partitioning of salt-soluble fission products into, and the absence of metal fuel constituents from, the salt phase. The salt sample will also be analyzed for lithium oxide concentration.

Equipment and Process Qualification

The aforementioned fuel preparations and HFDA test plans will be performed with unirradiated depleted uranium oxide fuel in order to qualify the equipment and process prior to introducing spent oxide fuel. This qualification will use all the prescribed equipment for fuel preparation and electrolytic reduction. The fuel basket will also be submitted to the Analytical Laboratory to qualify the developing analysis techniques.

TEST STATUS

At this writing, two bench-scale electrolytic reduction runs with unirradiated depleted uranium oxide have been performed in the

HFDA. The post-test analyses from the first two runs are in progress. Additional runs with unirradiated oxide fuel will be performed prior to introducing the spent oxide fuel. Thus far, the electrochemical responses from the HFDA runs with depleted uranium oxide are consistent with those reported previously.² Specifically, the cell operated within a range of approximately 0 to 100 mV above lithium potential at the cathode to 3.4 V above lithium potential at the anode. Current density ranged from approximately 1 A/cm² at the beginning of a run to 0.2 A/cm² at the end of a run.

ACKNOWLEDGMENTS

This work was supported under U.S. Department of Energy contract W-31-109-Eng-38.

REFERENCES

1. E. J. Karell, K. V. Gourishankar, "Electrometallurgical Treatment of Oxide Spent Fuel – Engineering-Scale Development," Proc. of the American Nuclear Society Topical Meeting on DOE Spent Nuclear Fuel and Fissile Material Management, Charleston, SC (September 1998).
2. K. Gourishankar, L. Redey, and M. Williamson, "Electrochemical Reduction of Metal Oxides in Molten Salts", Light Metals, ed., W. A. Schneider, Warrendale, PA, The Minerals, Metals, and Materials Society (2002).
3. J. P. Adams, B. R. Dabell, *Characteristics of UO₂-Zr Fuel Rods Irradiated in the BR3 Reactor*, EG&G Idaho, Inc. (November 1984).